Physical Cleaning of High Carbon Fly Ash

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KEYWORDS: fly ash, agglomeration, unburned carbon, and combustion by-products

ABSTRACT

An industrial fly ash sample was cleaned by three different processes, which were triboelectrostatic separation, ultrasonic column agglomeration, and column flotation. The unburned carbon concentrates were collected at purities ranaging up to 62 % at recoveries of 62 %. In addition, optical microscopy studies were conducted on the final carbon concentrates to determine the carbon forms (inertinite, isotropic coke and anisotropic coke) collected from these various physical-cleaning processes. The effects of the various cleaning processes on the production of different carbon forms from high carbon fly ashes will be discussed.

INTRODUCTION

Power requirements in the 21st century will demand environmentally clean and cost effective fuels for the generation of electricity within the world economic. Coal is our most abundant fossil fuel in the US and therefore will play a critical role as a major source of energy in the 21st century [1]. However, electricity generated by coal combustion results in increased emission of air pollutants such as NO_x and SO_x into the atmosphere, which leads to an increase in the formation of smog and acid rain. The Clean Air Act of 1990 requires the reduction of these gases into the atmosphere, and has led to the application of low-NOx burners and catalytic reduction systems in the utility industry. Although low-NOx burners and catalytic reduction systems are effective for the reduction of NOx, they often cause an increase in the amount of carbon remaining in the coal combustion by-products (CCBs) generated under these conditions [2,3]. These CCBs mainly consist of fly ash with high loss-on-ignition (LOI) carbon concentrates produced by the lower combustion temperatures required for the operation of the low-NO_x burners. Due to the limited applications of these high carbon fly ashes, they are being placed in landfills, which is also detrimental to the environment. Consequently, it is critical that new technologies be developed that will allow these high carbon fly ashes to be utilized more efficiently.

The Portland cement concrete industry uses fly ashes with the LOI values less than 6 %. The guideline for these types of fly ashes is summarized in the ASTM C-618 [4] standard. However, these ASTM standard only gives estimated LOI values for the production of stable Portland cement mixtures [5-7].

Petrologic analyses [8] of these high-carbon fly ashes have shown that the unburned carbon concentrates can be identified into three basic carbon forms. Using optical microscopic methods the three forms of carbon that can be identified are: (1) inertinite particles, (2) isotropic coke, and (3) anisotropic coke. In order to develop new applications for these carbon concentrates, they must be physically collected from these high LOI fly ashes. The three separation processes used for the collection of these carbon concentrates were triboelectrostatic separation [9], ultrasonic column agglomeration [10],and column flotation [11]. Consequently, the effects of the various cleaning processes on the collection of different carbon concentrates from high LOI fly ashes will be described within this paper. In addition, a more comprehensive report on this research is now being summarized in an ACS chapter book[12].

EXPERIMENTAL

Samples: A high LOI fly ash sample derived from the combustion of a bituminous coal at the Reliant Energy plant located in Shawville, PA was selected for this study. Analytical data for this sample are shown in Table 1.

Table 1: Analytical Data of Shawville Fly Ash (Dry weight basis)

Leco Furnace Analysis	
Moisture	0.26 %
Ash	82.27 %
LOI Carbon	17.73 %
Major Elemental Analysis	
Hydrogen	0.17 %
Nitrogen	0.18 %
Sulfur	0.35 %
Oxygen	3.45 %

Operating Conditions: Triboelectrostatic Separator

The tribo parallel plate separator used for this study consists of a venturi feed system driven by nitrogen pressure, an injection nozzle, and a high voltage separation section (Figure 1). The fly ash particles pass through the venturi feeder and become charged in this turbulent flow zone by contact with the copper tubing and with one another. The contact of the particles with copper surfaces, especially in the turbulent zone of the in line static mixer, results in effective charging of both unburned carbon and mineral. These charged particles then are forced out the nozzle in a ribbon of entrained particles approximately 7.62 x 0.3175 cm. This plume of particles is directed between two parallel charged plates 15.24 cm long and 7.62 cm apart. For fly ash separations this unit is operated + or - 25,000 volts on the separator plates. The positively charged unburned carbon particles are attracted to the negative electrode and the negatively charged mineral particles are moved to the positive electrode. A splitter is placed 15.24 cm downstream from the nozzle to separate the unburned carbon rich and ash rich fractions and directs them to two collection cyclones. The entire separator is swept with laboratory air by applying vacuum to the outlets of the collection cyclones. Sweep flow enters the separator through flow straighteners around the nozzle to control the flow in the separator section. This separator has a capacity of about 8 Kg/hr in continuous operation and can be used in the batch mode using as little as 100g fly ash feed. The recovery efficiency of the cyclones is typically greater than 95%. The concentrated unburned carbon (attracted to the negative electrode) generated in these runs, together with the feed, are then analyzed for carbon and ash contents.

Operating Conditions: Six-foot Ultrasonic Agglomeration Column Equipment

The types of ultrasonic treatments that were applied to the cyclohexane/ash slurry consisted of (1) a treatment during the preconditioning stage in the mix tank and (2) treatment within the column during operation of this agglomeration process. The ultrasonic wave was applied to the slurry mixture in the mix tank and column through the combination of a transducer from NDT, Inc. coupled with an M90 Reflectoscope from Automation/Sperry Inc., producing a wave in the frequency range of 0 to1 MHz.

<u>Column Batch Mode Operating Conditions:</u> Figure 2 shows the operational flow chart for the six-foot ultrasonic agglomeration column that was tested under batch mode conditions. As shown in Figure 2, the experimental setup consisted of a six-foot by four inch Plexiglas column, equipped with a variable speed electrical motor, a slurry mix tank equipped with variable speed air motor, a solvent recovery tank, and a 60-mesh stainless steel screen. Initially, the cyclohexane and fly ash slurry was prepared at about a 5:1 weight ratio and preconditioned for one minute before it was exposed to a 0.5 MHz ultrasonic wave for an additional minute. The preconditioned slurry was pumped into the column at the feed rate of 930 ml/min with the column ultrasonic wave frequency maintained at 1.0 MHz at a 2000 Hz pulse rate. During the course of these tests the agitation speed was maintained at 200-rpm with airflow of 189 cc/min. The carbon concentrate was collected on a 60-mesh screen, air-dried and analyzed to determine its purity. All of the carbon recoveries were calculated on a total weight carbon basis.

Operating Conditions: 2” Flotation Column

Separation of the carbon from the ash in this fly ash sample was evaluated using a release analysis method and 2” column flotation. The release analysis method used was the VPI Reverse Release Analysis [13].

This method is similar to Dell’s release analysis, but in “reverse”. The sample is first floated in a Denver cell to exhaustion, followed by the concentrate being re-floated to exhaustion two more times with the tailings being combined. The concentrate that remains is again placed in a Denver cell and floated at a fairly severe (high aeration and impeller rate) condition. The tailings are saved separately and the concentrate again placed in a Denver cell. This flotation and saving of the tailings is repeated with each subsequent test being at lower severity conditions (i.e. lower aeration and/or impeller rates). This procedure produced six tailings samples and one concentrate sample.

As shown in figure 3, the continuous 2” column flotation tests were run in an 80-inch long 2-inch I.D. column. The column tests were run at increasing slurry feed rates with concentrate, tailings, and feed samples collected at each feed rate once the column reached steady-state operation. The use of increasing slurry feed rates allows grade-recovery curves to be developed from these results.

Petrologic Analysis Procedure

Petrologic analyses were conducted using a Zeiss Universal research microscope at 800x magnification and with an objective under oil immersion. The samples were prepared into petrologic briquettes by mixing them with an epoxy resin. Typically between 400-860 microscopic field areas were taken on each fly ash sample. The unburned carbon particles were classified according to prior petrologic examinations conducted on a number of high LOI fly ashes, that have shown that the unburned carbon is not visually uniform and identified three microscopically distinct carbon types: (i) inertinite particles, which appear to be non-fused particles; (ii) isotropic coke; and (iii) anisotropic coke, the latter two being extensively reacted particles, which appear to have passed through a molten stage [14]. In addition, carbonaceous particles that consist of fragments of less than 10 um are classified as fragments [15]. The above particle types were further subdivided according to particle shape, pore volume, and wall thickness. Furthermore, inorganic particles were classified as either glass (solid and frothy non-crystalline aluminosilicates, including glassy cenospheres), quartz (non-melted silicates), mullite (orthorhombic mineral with a typical composition $Al_6Si_2O_{13}$), and spinel (iron oxides) [16].

RESULTS AND DISCUSSION

Initially, the Shawville fly ash was wet screened to determine its particle-size distribution. It was determined that the unburned carbon was distributed through out all of the size fractions of this sample. Even though there was a slight concentration of the carbon particles in the 200-mesh range, this size fraction was too narrow to merit the prescreening of the sample. Consequently, there was no advantage to prescreening the sample to isolate carbon-rich fractions before any cleaning process was applied. The wet screening results are shown in Table 2.

Table 2: Size Analysis of Shawville Fly Ash.

Mesh Size	Wt. % Retained	Cumulative wt. %	Ash %	Cumulative Ash %
50	0.1	0.1	74.4	74.4
50 x 100	3.1	3.3	46.5	47.8
100 x 200	15.2	18.4	61.9	59.4
200 x 325	13.5	31.9	70.4	64.0
325 x 500	19.0	46.3	75.3	68.3
500 x 0	49.2	100.00	81.7	74.9
Sum	100.00			

The actual performance of the single stage cleaning processes for the separation of the unburned carbon concentrates from this Shawville fly ash are shown Table 3.

Table 3: Summary of the Cleaning Processes for Shawville Fly Ash (LOI carbon 17.73 %)

Separation Process	% LOI Carbon	% Carbon Recovery
Triboelectrostatic	27.52	49.95
Ultrasonic Column Agglomeration	53.23	54.54
Column Flotation	61.22	62.34

It was determined that the most effective cleaning process for this Shawville fly ash was the flotation which resulted in a LOI carbon value of 61% at a carbon recovery of 62%. Under these flotation conditions, the ash product was approximately 8.5% carbon which is unacceptable for utilization in the Portland cement industry (refer to Figure 4). It is assumed that the low cleaning performance can be attributed to the fact that approximately 50% of the carbon are less than minus 500 mesh. For the triboelectrostatic process the presence of fine particles will have a direct effect on the charging and collecting properties used in this separation process. This is an indication that sizing may be an important parameter, however, it was not examined during the course of this study.

The potential separation performance was determined by the reverse release analysis. As shown in figure 4, the best performing process for the recovery of unburned carbon from fly ash was column flotation followed by agglomeration and then triboelectrostatic. However, in all cases there is room for significant improvements in the cleaning performance of these separation processes. The cleaning on this fly ash may require multistage cleaning circuits for the production of cleaner ash
($\leq$ 6% LOI) and carbon ($\geq$ 60% LOI) products.

The elemental analysis (refer to Figure 5) of the carbon concentrates show that all cleaning processes resulted in similar products with the exception of the ones collected from the triboelectrostatic process. In this sample, there was an increase in the amounts of iron oxides and a reduction of aluminum and silicon oxides. The triboelectrostatic process is based on the ability of the fine particles to pick up a surface electrical charge, which allows them to be collected or repelled through the separator. Consequently, the triboelectrostatic process resulted in carbon concentrates with different inorganic compositions.

Before conducting the petrologic analysis of the carbon concentrates, additional carbon concentrates were collected under similar conditions by the triboelectrostatic, ultrasonic column agglomeration, and column flotation processes. The type of separation processes and carbon contents of the resulting concentrates are summarized in Table 4.

Table 4: Separation and Characterization of Carbon Concentrates.

Samples	**Separation Process**	**# of Stages of Separation**	**% LOI Carbon**
Shawville Fly Ash	None	None	17.7
Tribo-carbon	Triboelectrostatic	Two	35.0

Agglomeration-carbon	Column Agglomeration	One	48.6
Flotation-carbon	Column Flotation	One	48.2

The petrologic data for the samples shown in Table 4 are summarized in Table 5. For all of the samples investigated, the anisotropic carbon was determined to be the dominant type of carbon present in these samples.

Table 5: Petrologic Analysis of the Carbon Particles of the Shawville Fly Ash and Carbon Concentrates.

Sample	Anisotropic/ Vol %	Isotropic/ Vol %	Inertinite/ Vol %	Fragments < 10um/ Vol %
Shawville Fly Ash	68.1	1.0	9.8	21.1
Tribo-carbon	47.8	1.2	10.6	40.4
Agglomeration-carbon	73.7	0.8	13.9	11.6
Flotation-carbon	63.2	0.5	11.0	25.3

The parent Shawville fly ash sample and the carbon sample enriched using the flotation column present very similar concentrations of the different carbon particles, indicating that this separation method tend to preserve the concentrations of the particles present in the parent fly ash sample, without discriminating against any particular type. In contrast, the carbon concentrate samples produced using the triboelectrostatic separator and the agglomeration column present different concentrations of anisotropic carbon as well as fragments than those observed in the parent sample. The carbon sample concentrated by using the agglomeration method presents a smaller concentration of fragments than the parent sample (11.6 vs. 21.1, Table 5), indicating that the agglomeration method is somewhat more selective towards larger particles. In contrast, the carbon sample that was obtained by triboelectrostatic separation has a much larger concentration of fragments (40.4 vs. 21.1, Table 5), that could be due to a more selective beneficiation of smaller particles as well as some particles being broken during the separation process itself.

The inorganic fraction of the parent fly ash sample is dominated by aluminosilicate particles and spinel minerals that are present in smaller sizes than most of the carbon particles. The above trends observed for the carbon particles also apply to the inorganic particles of the observed materials. The sample obtained by flotation preserves the character of the parent fly ash sample, while the sample obtained by agglomeration has larger inorganic particles, and in contrast, the sample separated by the triboelectrostatic method exhibits much larger concentration of smaller inorganic fragments. Furthermore, the inorganic fraction observed in the two fly ash samples with the highest carbon content (i.e. those obtained by agglomeration and flotation) is intimately associated with carbon fraction. Furthermore, these mixed carbon/mineral particles have a smaller particle size than the carbonaceous particles. Finally, the sample obtained by triboelectrostaic separation has somewhat larger concentration of spinel particles.

CONCLUSIONS

Column flotation was determined to be the most effective process for the collection of carbon concentrates at a LOI value of 61% and a carbon recovery of 62% with 90% of the ash reporting to the tails with LOI values < 8% for the Shawville fly ash. However, in all cases there is room for significant improvement in the cleaning performance of these separation processes. The cleaning on this Shawville fly ash may require multistage cleaning circuits for the production of cleaner ash ($\leq$ 6% LOI) and carbon ($\geq$ 60% LOI) products. The optical microscopy studies have shown that the flotation column tends to preserve the concentrations of the particles present in the parent fly ash sample, without discriminating against any particular type. In contrast, the carbon concentrate samples produced using the triboelectrostatic separator and the agglomeration column present different concentrations of anisotropic carbon as well as fragments than those observed in the parent sample.

Reference:

1. Song, C., and Schobert, H. H., 1996, Fuel, **75**, 724.
2. Maroto-Valer, M. M., Taulbee, D. N., and Hower, J. C., 1998, Prepr. Am. Chem. Soc. Div. Fuel Chem., **43**, 1014.
3. Stewart, B., 1998, 15 th Annual International Pittsburgh Coal Conference, **CD volume 1-9**.
4. ASTM C-618, "Standard Specification for Fly As and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Potrland Concrete".
5. Hill, R. L., Sarkar, S. L., Rathbone, R. F., and Hower, J. C. Cem. Concr. Res. 1997, **27**,193.
6. Freeman, E, Goa, Y. M., Hurt, R. H., and Suuberg, E, M., Fuel, 1997, **8**, 761.
7. Gao, Y., Shim, H., Hurt, R. H., and Suuberg, E. M., Fuel, 1997, **11**, 457.
8. Hower, J. C., Rathbone, R. F., Graham, U. M., Groppo, J. G., Brooks, S. M., Robl. T. L., and Medina S. S., Proc. Int. Coal Testing Conf. 1995, 49.
9. Soong, Y., Schoffstall, M. R., Irdi, G. A., and Link, T. A., Proc. 1999 International Ash Utilization Sym. P548, 1999.
10. Gray, M. L., Champagne, K. J., Soong, Y., and Finseth, D. H., 1999, 16th Annual International Pittsburgh Coal Conference, **CD volume**.
11. Killmeyer, R. P., Ciocco, M.V., Zandhuis, P.H., "Development of a Procedure for Determining the Floatability Potential of Fine Coal," Proceedings; 17th International Coal Preparation Exhibition & Conference, May 3rd 2000, pp. 291-312.
12. Gray, M. L., Champagne, K. J., Soong, Y., Killmeyer, R. P., Baltrus, J., Maroto-Valer, M. M., Andersen, J. M., Ciocco, M.V., and Zandhuis, P.H., ACS Chapter Book, " Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21 st Century", unpublished.
13. Killmeyer, R. P., Ciocco, M.V., Zandhuis, P.H., "Development of a Procedure for Determining the Floatability Potential of Fine Coal," Proceedings; 17th International Coal Preparation Exhibition & Conference, May 3rd 2000, pp. 291-312.
14. Maroto-Valer, M. M., Taulbee, D. N., and Hower, J. C., 1999, Energy & Fuels, **13**, 947.
15. Bailey, J. G., Tate, A., Diessel, C. F. K., and Wall, T.F., Fuel, 1990, **69**, 225.

16. Hower, J. C., Rathbone, R. F., Graham, U. M., Groppo, J. G., Brooks, S. M., Robl, T. L., and Medina, S. S., Proceedings International Coal Testing Conference, 1995, p. 49.

Acknowledgements:
We wish to thank Reliant Energy for providing the Shawville fly ash sample.

Figures

Figure One: Schematic Drawing of Triboelectrostatic Separator.

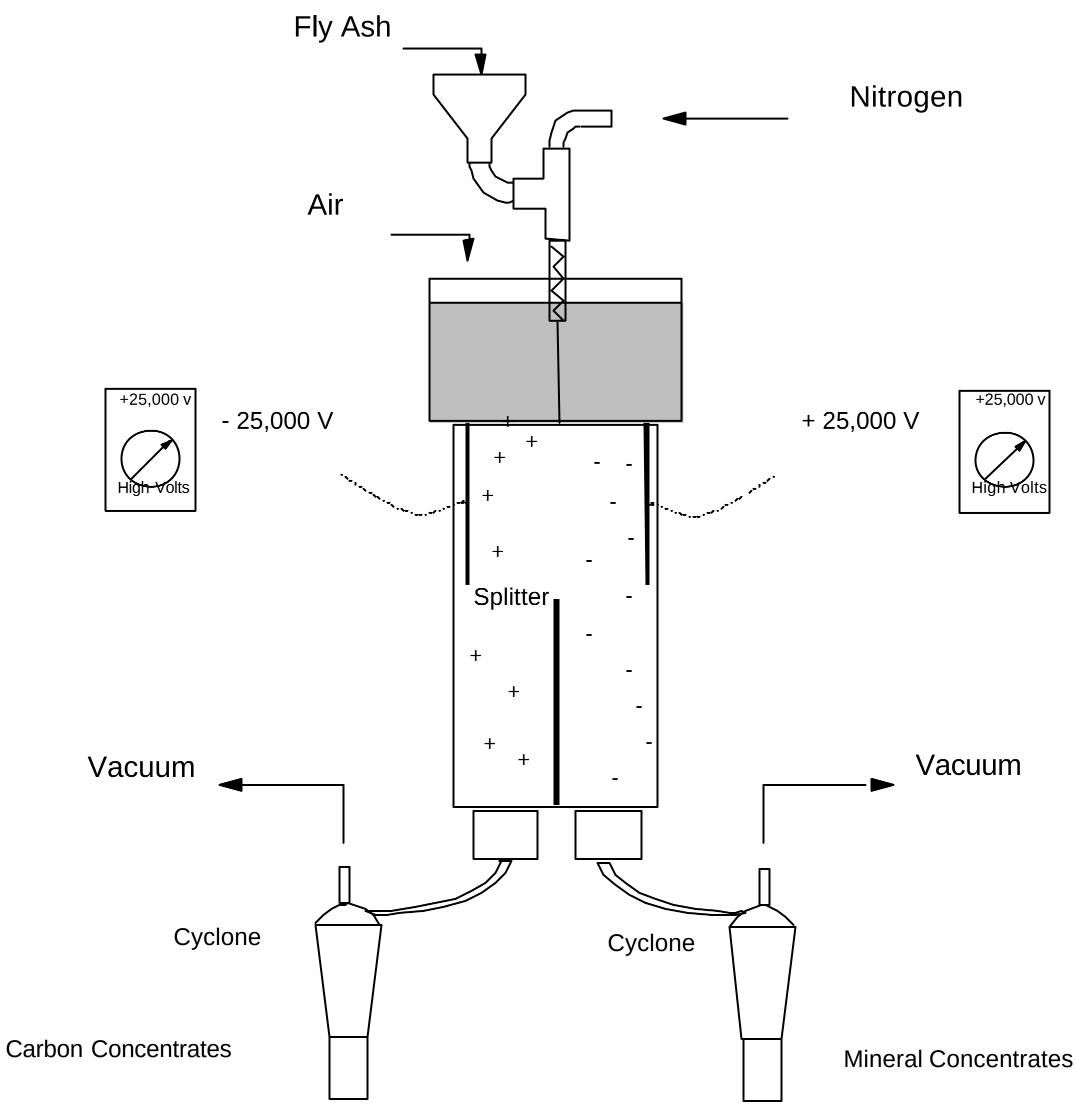

Figure Two: Schematic Drawing of Ultrasonic Agglomeration Column System.

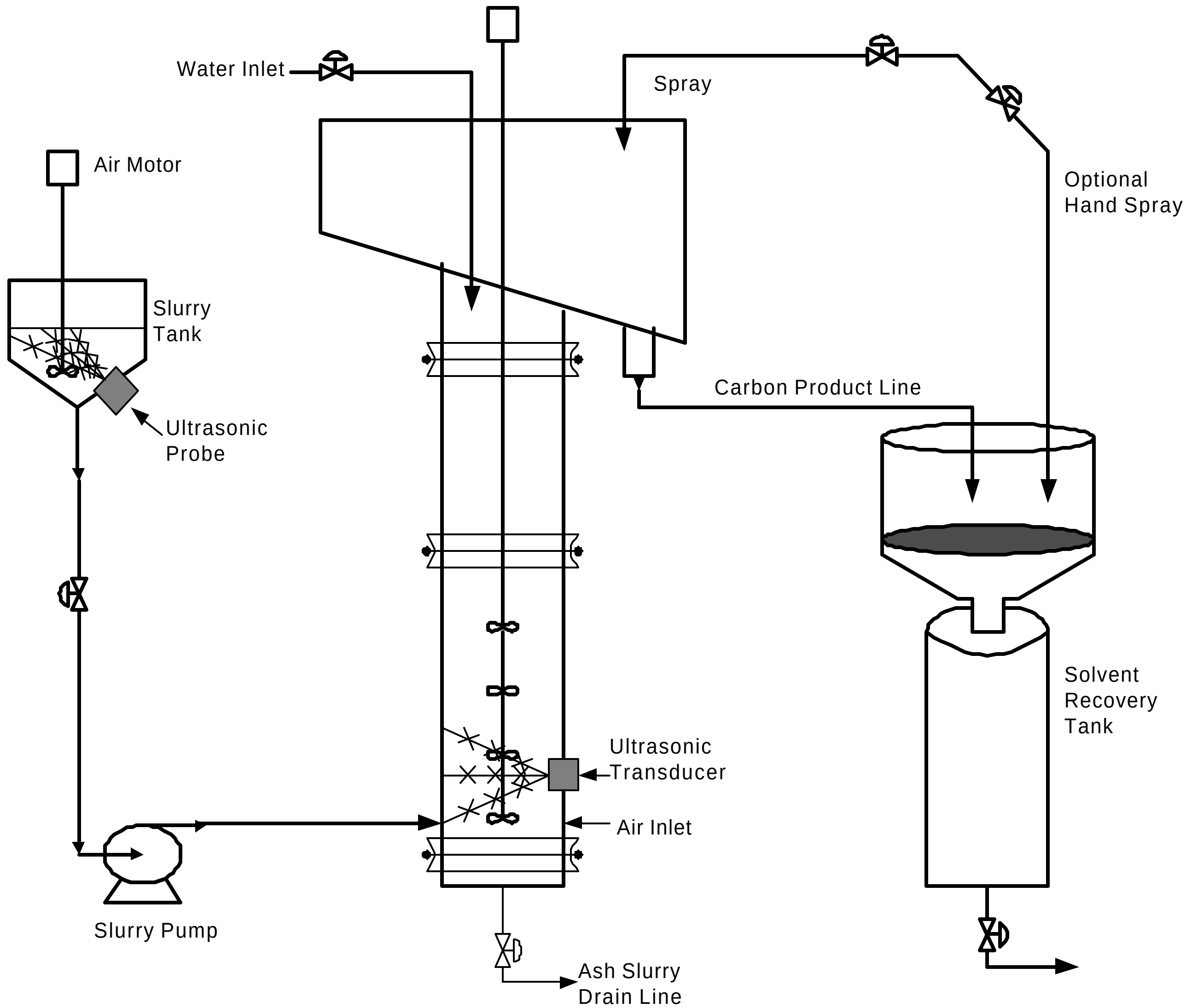

Figure Three: Schematic Drawing of Column Flotation System.

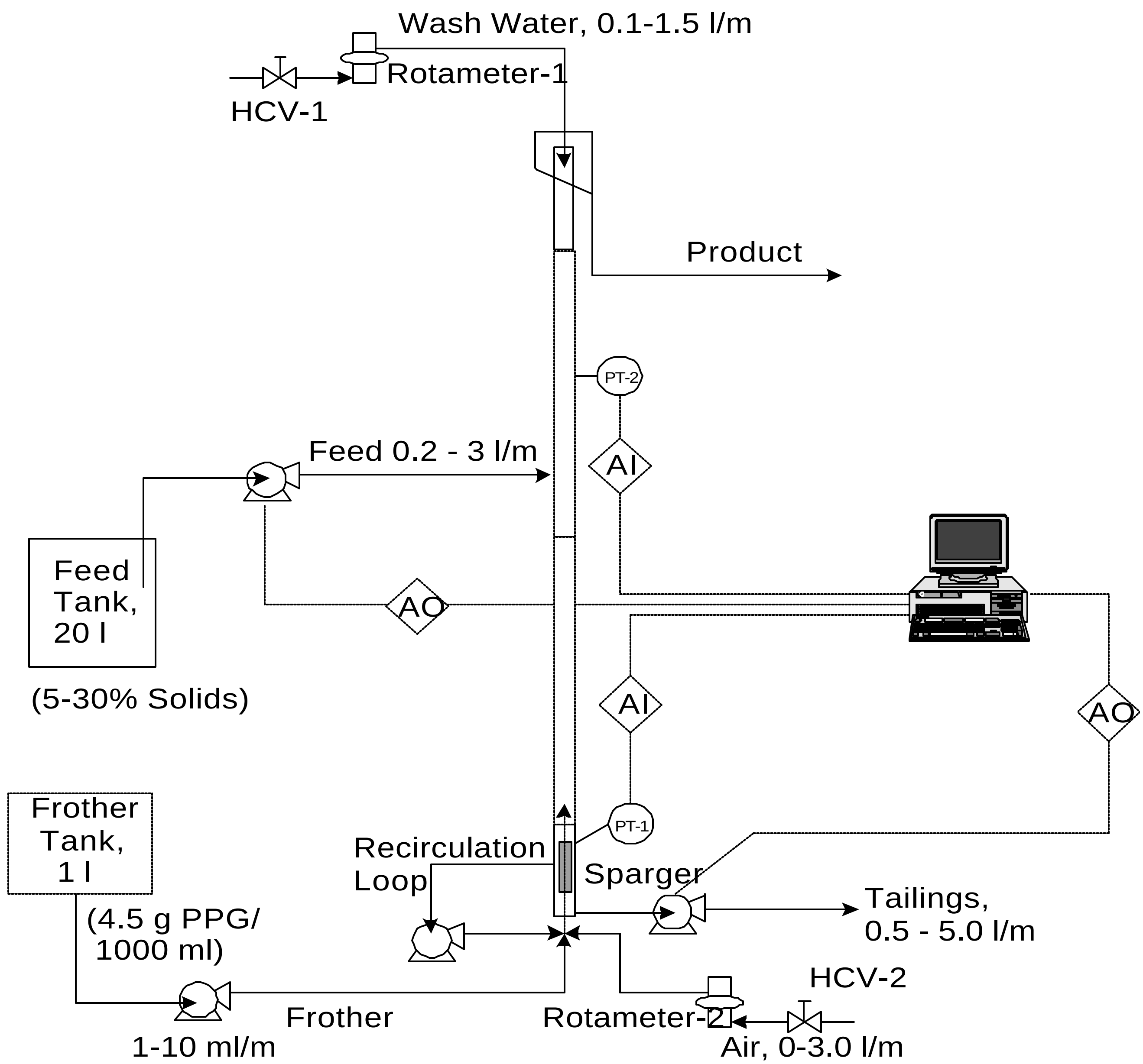

Figure Four: Summary of the Performance Analysis of Shawville Fly Ash.

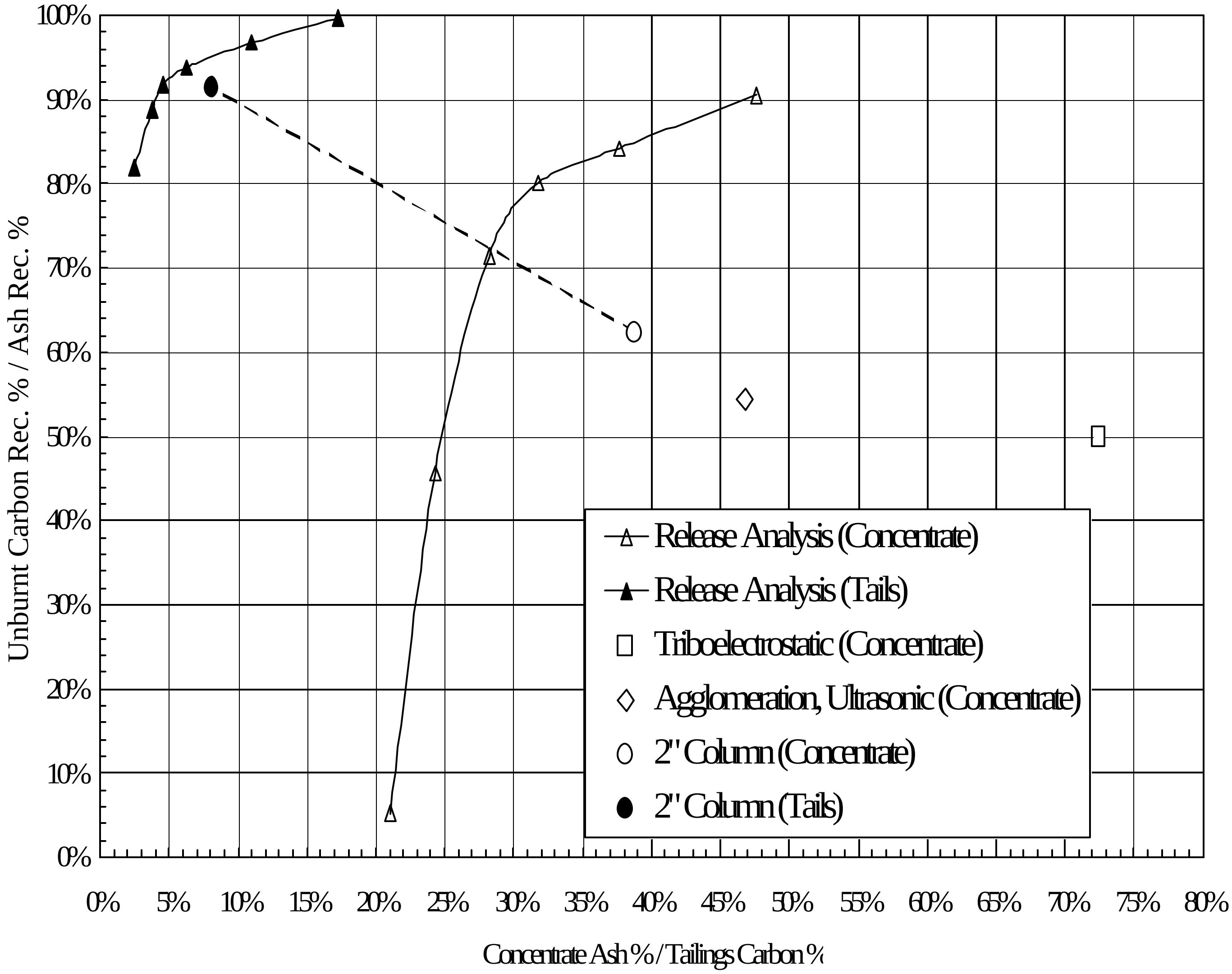

Figure Five: Major Elemental Analysis of Shawville Fly Ash Carbon Products Collected by Various Methods.